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(54) ARTICLES OR PARTS OF NICKEL-CHROMIUM OR NICKEL-CHROMIUM-IRON ALLOYS

(71) We, INTERNATIONAL NICKEL LIMITED, a British Company, of Thames House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Various articles such as pressure vessels, heat exchangers and steam generators, or parts of such articles are exposed in use to high-purity water under pressure at elevated temperatures. These articles and parts can advantageously be made of nickel-chromium or nickel-chromium-iron alloys, for example alloys containing from 75 to 80% nickel, 14 to 16% chromium and up to 8% iron.

Investigations of the behaviour of these alloys have shown that under certain conditions, namely contamination of the water with oxygen and the presence of crevices in the surface, intergranular cracking could occur as a result of stress-corrosion attack. It was found that certain nickel-chromium and nickel-chromium-iron alloys, containing from 14 to 35% chromium and 0 to 25% iron, (with the proviso that when the iron content exceeds 0.5% the cromium content is at least 20%) one or both of titanium and aluminium in amounts not exceeding 0.5% each. from 0 to 1% silicon, from 0 to 0.15% carbon, and from 0 to 7.7% molybdenum and from 0 to 1.2% tantalum (with the proviso that when molybdenum or tantalum is present the chromium content is at least 20%) the balance, apart from impurities and residual deoxidants, being nickel, had increased resistance to this form of attack, and the use of such alloys for articles and parts exposed in use to high-purity water at elevated temperature and pressure is described and claimed in our specification No. 1,114,996.

It has now been found that many alloys that are resistant to intergranular cracking in high-purity water, even if it is aerated, are subject to cracking in water that is contaminated with lead although otherwise of high purity, even if this water is deaerated; the cracks that form under these conditions being transgranular. Although rigid precautions are taken to exclude lead from hot water systems of nuclear reactors, e.g. by the use of lead-free pipe joint compounds, it would obviously be desirable to have available an alloy which exhibited substantial resistance to stress-corrosion cracking in pressurised water whether it was contam-

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inated by lead or air, or both, and whether surface defects were present in the material or not. It is our object in this invention to provide such an alloy.

Articles and parts that are exposed at elevated temperature and pressure, e.g. 150 to 350°C, to high-purity water liable to contamination by lead are made according to the invention, from nickel-chromium and nickel-chromium-iron alloys containing from 52 to less than 67% nickel, from 26 to 32% chromium, from 0 to 10% molybdenum, from 0 to 6% niobium, from 0 to 10% vanadium and from 0 to 10% tungsten, with the provisos (i) that the sum of the contents of molybdenum, niobium, vanadium and tungsten does not exceed 15%, and (ii) that the contents of chromium, iron, molybdenum, niobium, vanadium and tungsten are so correlated that the sum

$$(\%Cr) + 0.25(\%Fe) + 0.9(\%Mo) + (\%Nb) + 1.25\,[(\%V) + (\%W)]$$

(hereinafter referred to as SC), is at least 28%, from 0 to 0.1% carbon, from 0 to 5% titanium, from 0 to 5% aluminium, from 0 to 2% manganese and from 0 to 2.5% silicon. Any balance (apart from impurities) is iron.

It is important that the nickel content does not equal or exceed 67%, since for reasons that are not fully understood larger amounts of nickel apparently promote stress-corrosion cracking (or at least do not assist in overcoming or suppressing such cracking) in the presence of lead, an effect not experienced in aerated pressurised water. Preferably the nickel content does not exceed 65%. At least 52 and preferably at least 55% nickel must be present to provide satisfactory mechanical and other characteristics, and to ensure good resistance to chloride stress-corrosion cracking.

Both chromium and, to a lesser extent, iron contribute to the resistance of the alloys to stress-corrosion attack in the presence of lead. To ensure freedom from this form of attack the chromium content must be at least 26% and advantageously is at least 27%. As the chromium content increases above this level, however, there is an increasing tendency for scale to form on the surface of the alloys in the presence of lead. This can have serious effects in a nuclear reactor, since with time the scale exfoliates and forms a sludge. The chromium content must therefore not exceed 32%, and is preferably not more than 30%. Iron restricts or inhibits the tendency for scale to form at the higher chromium contents, and preferably the alloys contain at least 4% and most advantageously from 8 to 20% of iron. When the chromium content is 28% or more quite severe scaling may occur if the iron content is less than 8% unless the chromium and iron contents are so related that (%Cr) − 0.5(%Fe) does not exceed 28%. Reducing this difference by raising the proportion of iron to chromium decreases the incidence of scaling and preferably (%Cr) − 0.5(%Fe) is not more than 23%. Excessive amounts of iron and nickel combine to impair the resistance to stress-corrosion, and the combined content should therefore not be so great that

$$(\%Ni) + 0.7(\%Fe)$$

exceeds 70%.

Molybdenum, niobium, vanadium and tungsten also contribute to the resistance of the alloys to stress-corrosion in the presence of lead and also strengthen the alloys, and advantageously at least one of these elements is present in a total amount of at least 1%. If the combined content of chromium and iron as expressed by (%Cr) + 0.25(%Fe) is less than 28% one or more of these elements must be present so that the value of SC is at least 28%, and preferably the value of SC is at least 30.5%. Preferably the niobium content does not exceed 4% and the content of any one of molybdenum, vanadium and tungsten does not exceed 8%, and most advantageously the total content of all four of the last-mentioned constituents does not exceed 8%.

Aluminium and titanium in amounts up to 5% each also lessen the susceptibility of the alloys to cracking in the presence of lead, but large amounts of these elements, e.g. 3% or 4%, promote cracking by water containing dissolved air. Preferably therefore not more than 1% each of aluminium and titanium is present.

A preferred range of alloy compositions that would afford markedly improved resistance (compared with conventionally used compositions) to attack in high purity water contaminated with both air and lead, to attack in chloride media, and to scale formation in lead-contaminated water, contain from 26 to 30% chromium, from 62 to 65.5% nickel, from 0.01 to 0.06% carbon, up to 1% titanium, from 0 to 3% niobium and from 0 to 8% molybdenum, any balance, apart from impurities, being iron. An alloy containing 28% chromium, and from 8 to 13% iron, the balance, apart from impurities, being nickel has excellent resistance to cracking in high-purity water contaminated with lead, air, or chloride and also to scaling.

By way of example, alloys were prepared having the compositions set forth in Table I, in which Alloys 1 to 11 are in accordance with the invention and Alloys A to W are not. All the alloys were cast to ingots and reduced by forging and hot- and cold-rolling to flats 0.15 inch thick. The flats were annealed at 1150°C, water-quenched, and then machined into test blanks 3.25 inches long, 0.5 inch wide and 0.12 inch thick. Some test blanks of each alloy were

heated at 675°C for 2 hours and then air-cooled. This treatment rendered them more susceptible to stress-corrosion attack.

Each strip was formed into a U-bend test piece, the legs of which were held parallel by a bolt so that it was in a highly-stressed condition.

The test pieces were then subjected to stress-corrosion tests in which they were placed in autoclaves and immersed together with 10 grams of lead powder in distilled and deionized water. The water was deaerated, the autoclaves were sealed and the contents were heated to 315°C.

Tests were continued for a maximum of 8 weeks, the autoclaves being opened every 2 weeks and the test pieces inspected for cracks. Where cracking was visually observed under low magnification (x45) the test piece was removed and the depth of crack determined. The tests on the other specimens were resumed using fresh water and lead. Those specimens that did not show visible cracking at the end of 8 weeks were then examined metallographically.

The results are set forth in the last two columns of Table I. 'OK' indicates that no cracking was observed, the numeral in parentheses being the number of specimens tested. A notation such as '4/60' indicates that after 4 weeks a crack 60 thousandths of an inch deep was observed, and one such as '8m/110' indicates a crack observed on metallographic examination after 8 weeks and 110 thousandths of an inch deep.

TABLE I

Composition							Heat Treatment	
Alloy No.	Cr (%)	Fe (%)	Ni (%)	C (%)	Ti (%)	Other* (%)	Annealed plus H.T.	Annealed
1	30.7	10.2	58.3	0.06	0.15	—	OK(4)	OK(2)
2	27.2	10.3	61.7	0.07	0.14	—	OK(4)	8m/0.5; 8m/0.5 8m/3; 8m/4
3	28.4	18.8	52.7	0.05	0.21	—	—	OK(2)
4	28.7	14.2	56.3	0.05	0.21	—	—	OK(2)
5	27.6	3.0	65.6	0.05	0.26	0.9 Nb 0.9 W 1.0 Mo	—	OK(2)
6	27.7	3.2	65.6	0.06	0.29	2.8 Nb	—	OK(2)
7	27.9	2.5	65.0	0.04	0.15	3.6 V	—	OK(2)
8	26.3	4.2	66.5	0.06	0.30	1.9 W	—	OK(2)
9	27.0	4.4	66.4	0.06	0.33	1.8 V	—	OK(2)
10	27.2	11.8	58.4	0.06	0.20	1.9 Si	OK(2)	—
11	27.4	3.1	64.4	0.06	—	4.0 Ti	OK	—
A	24.1	8.2	67.0	0.11	0.17	—	8m/35; 8m/30	—
B	24.0	8.1	67.1	0.02	0.23	—	8m/15; 8m/20	—
C	22.4	9.4	67.9	0.10	0.19	—	8m/45; 8m/20	—
D	24.2	6.6	68.4	0.06	0.08	—	8m/10	8m/15; 8m/30
E	22.5	8.4	68.4	0.02	0.22	—	8m/50; 8m/55	—
F	23.5	5.7	69.5	0.05	0.27	—	8m/9	8m/10
G	20.8	8.8	69.6	0.03	0.21	—	8m/60; 8m/70	—
H	14.9	6.7	70.0	0.05	0.34	7.5 Mo	8m/85; 8m/42	8m/95; 8m/60
I	20.0	7.0	71.0	0.01	0.29	1.2 Ta	4/60	4/60
J	23.6	1.6	74.0	0.02	0.21	—	8m/45; 8m/35	—
K	24.8	0.1	74.3	0.06	0.30	—	8m/22	8m/10
L	24.2	0.3	74.6	0.09	0.21	—	8m/30(2)	—
M	15.9	7.3	75.0	0.06	0.28	0.9 Nb	4/80	2/60
N	20.7	0.1	78.4	0.02	0.25	—	8m/80(2)	—
O	24.0	12.9	62.5	0.05	0.16	—	8/100; 8/80	—
P	20.6	26.6	52.9	0.09	0.09	—	8/60; 8/80	8/40; 8/40
Q	20.2	16.4	62.8	0.05	0.13	—	8/100; 8/80	—
R	24.0	7.5	65.5	0.09	0.37	1.7 Mo	—	8m/8; 8/80 8/80
T	20.9	<0.1	67.0	0.06	0.11	5.9 Co	8/80	—
U	25.7	<0.1	66.9	0.05	0.12	6.6 Mn	8/80	—
V	27.1	<0.1	64.2	0.04	0.22	7.1 Cu	8/80	—
W	25.8	<0.1	64.8	0.05	0.15	8.2 Ta	8/100	—

* = Including 0.2% or less of each of silicon and manganese and generally 0.1% or less of each of aluminium and copper plus other impurities.
Nickel is by difference.

The results show that the only alloy in accordance with the invention that suffered any cracking was Alloy 2, and for this the cracks were very shallow and only appeared after the full period of test and in one condition of heat-treatment. In contrast, every alloy containing more than 67% nickel (and numerous others not reported) was cracked. No alloy for which the sum SC exceeded 28% (again excepting Alloy 2 for which the sum was 29.8) cracked, and all the alloys with this sum exceeding 30.5% were crack-free.

Many of the alloys A to W are in accordance with our specification No. 1,114,996 and are resistant to stress-corrosion cracking in high-purity water saturated with air but free from lead. Thus Alloys A, B, D and F have compositions similar to that of Alloys 1 and 2 of No. 1,114,996, and Alloys G, N, K, R and I are similar or identical to Alloys Nos. 3, 4, 5, 7 and 9 respectively of No. 1,114,996. It will be observed that all these alloys cracked badly in the presence of lead.

The results for Alloys T, U, V and W show that additions of cobalt, manganese, copper and tantalum do not confer resistance to cracking.

Several alloys were also subjected to tests in which the extent of scaling in lead-contaminated and lead-free water was determined by means of the weight loss after 14 days exposure, the alloys being prepared and tested as in Table 1. Alloys AA to EE are not in accordance with the invention, and comparison of these alloys with Nos. 1, 3, 7 and 10 in accordance with the invention clearly shows the scale-inhibiting effect of iron. The results are set forth in Table II.

TABLE II

	Composition						Weight loss (MDD)	
Alloy No.	Cr (%)	Fe (%)	Ni (%)	C (%)	Ti (%)	Other (%)	Lead-Contaminated	Lead-Free
AA	35.0	1.1	63.3	0.05	—	—	85.0	0.17
BB	29.5	0.1	69.7	0.03	0.22	—	8.3	0.08
CC	31.4	2.3	67.5	0.05	0.30	—	32.4	—
DD	29.8	0.2	67.1	0.04	1.8	0.7 Al	30.8	—
1	30.7	10.2	58.3	0.06	0.15	—	1.5	0.14
10	27.2	11.8	58.4	0.06	0.20	1.9 Si	1.0	—
EE	27.5	0.1	72.0	0.06	0.18	—	4.4	—
7	27.9	2.5	65.0	0.04	0.15	3.6 V	6.0	—
3	28.4	18.8	52.7	0.05	0.21	—	0.8	—

MDD = Milligrams per Square Decimeter Per Day.

Many alloys which may be used in the invention and which contain one or more of molybdenum, niobium, tungsten and vanadium have tensile and proof strengths from 50% to 100% greater than those of a conventionally-used alloy containing 16% chromium, 6.7% iron, 0.05% carbon, balance nickel, in both the annealed and aged conditions. Since these alloys offer a high degree of resistance to stress-corrosion cracking, it follows that they can withstand a much greater stress han conventionally-used alloys without cracking.

Some alloys used according to the invention were also tested for susceptibility to stress-corrosion cracking in chloride environments, using the well-known boiling magnesium chloride test. Three specimens each of Alloys 3 and 4, which alloys contain over 50% nickel were solution-treated at 1150°C for one hour, water-quenched, held at 675°C for two hours and air-cooled. They were then formed into U-bends and immersed in boiling magnesium chloride (154°C) in an autoclave for a period of 30 days. None of the specimens cracked. In contrast, a similarly heat-treated and tested alloy which contained 42.2% nickel, 28.8% chromium, 28.0% iron, 0.05% carbon and minor amounts of aluminium, titanium and

impurities exhibited cracking in each of three specimens tested, the crack depths ranging from 20 to 60 thousandths of an inch.

The articles and parts with which the invention is concerned include heat exchangers, pressure vessels, tubing and primary water piping.

WHAT WE CLAIM IS:—

1. An article or part exposed at elevated temperature and pressure to high-purity water liable to contamination by lead and made from a nickel-chromium or nickel-chromium-iron alloy containing from 52 to less than 67% nickel, from 26 to 32% chromium, from 0 to 10% molybdenum, from 0 to 6% niobium, from 0 to 10% vanadium and from 0 to 10% tungsten, with the provisos (i) that the sum of the contents of molybdenum, niobium, vanadium and tungsten does not exceed 15%, and (ii) that the contents of chromium, iron, molybdenum, niobium, vanadium and tungsten are so correlated that the sum

$$(\%Cr) + 0.25(\%Fe) + 0.9(\%Mo) + (\%Nb) + 1.25\ [(\%V) + (\%W)]$$

is at least 28%, from 0 to 0.1% carbon, from 0 to 5% titanium, from 0 to 5% aluminium, from 0 to 2% manganese and from 0 to 2.5% silicon, any balance (apart from impurities) being iron.

2. An article or part according to claim 1 in which the nickel content of the alloy is from 55 to 65%, the chromium content is from 27 to 30%, and the titanium and aluminium contents do not exceed 1% each.

3. An article or part accordling to claim 1 or claim 2 in which the sum

$$(\%Cr) + 0.25(\%Fe) + 0.9(\%Mo) + (\%Nb) + 1.25\ [(\%V) + (\%W)]$$

in the alloy is at least 30.5%.

4. An article or part according to any preceding claim in which the alloy contains at least 4% iron.

5. An article or part according to claim 4 in which the alloy contains 8 to 20% iron.

6. An article or part according to any preceding claim in which the chromium and iron contents in the alloy are so related that

$$(\%Cr) - 0.5(\%Fe)$$

does not exceed 28%.

7. An article or part according to any preceding claim in which the alloy contains at least 1% in total of one or more of molybdenum, niobium, vanadium and tungsten.

8. An article or part according to claim 7 in which the niobium content of the alloy does not exceed 4% and the content of any one of molybdenum, vanadium and tungsten does not exceed 8%.

9. An article or part according to claim 8 in which the total content of niobium, molybdenum, vanadium and tungsten in the alloy does not exceed 8%.

10. An article or part according to claim 1 in which the alloy contains from 26 to 30% chromium, from 62 to 65.5% nickel, from 0.01 to 0.06% carbon, up to 1% titanium, from 0 to 3% niobium and from 0 to 8% molybdenum, the balance, apart from impurities, being iron.

11. An article or part according to claim 1 in which the alloy contains 28% chromium and from 8 to 13% iron, the balance, apart from impurities, being nickel.

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